

SYNTHESIS OF Tin (IV) DICHLORIDE HEXADECAFLUOROPHTHALOCYANINE (SnPcCl₂F₁₆) AS SEMICONDUCTOR MATERIAL FOR ORGANIC THIN FILM TRANSISTORS

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An axially coordinated Tin (IV) Dichloride hexadecafluorophthalocyanine (SnPcCl₂F₁₆) was synthesized. The electron energy level was studied by UV-vis absorption and cyclic voltammetry methods. The measurement results indicated that the SnPcCl₂F₁₆ compound embody suitable lowest unoccupied molecular orbital level for electron injection. Thermal analysis showed the compound has excellent thermal stability with decomposition temperature above 470 °C. The SnPcCl₂F₁₆/*p*-6p (SnPcCl₂F₁₆ on *p*-sexiphenyl) organic thin film transistors (OTFTs) using SnPcCl₂F₁₆ as an active layer and *p*-6p as an inducing layer was fabricated by the physical vapor deposition technique. The SnPcCl₂F₁₆ semiconductor film was characterized by XRD and AFM. And the results indicated that SnPcCl₂F₁₆ molecules can be oriented after the employment of the *p*-6p inducing layer. Charge carrier field-effect mobility (μ) and threshold voltage (V_T) of the SnPcCl₂F₁₆/*p*-6p OTFTs were $0.85 \times 10^{-3} \text{ cm}^2/\text{V s}$ and 7.62 V, respectively.

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1. Introduction

Phthalocyanines are organic pigments with good environmental stabilities, narrow HOMO-LUMO gap, and their characters can be tuned by the choice of central metal and the introduction of various peripheral substituents [1]. Thus, phthalocyanine compounds attract much attention and they have been studied for various applications, such as nonlinear optics, information storage systems, chemical sensors, display devices [2].

Most of the unsubstituted phthalocyanines show the characteristics of *p*-type semiconductor while some metal hexadecafluorophthalocyanines, such as CuPcF₁₆, exhibit air-stable *n*-type semiconducting behavior due to their electron-transporting characteristics. These properties of MPcF₁₆ result in a number of studies aiming at different applications like gas sensors photovoltaic cells, and rectifying junction [2]. Although synthesis of fluorinated copper, cobalt, zinc, ruthenium phthalocyanines has long been reported [3-5], an interest in the study on the properties of these compounds is rekindled. Basova et al investigated the chemical properties of CuPcF₁₆ and found the compound has lower volatility than its unsubstituted analogue [2]. The synthesis and films structure features of hexadecafluorosubstituted vanadyl phthalocyanine (VOPcF₁₆) were reported in reference literature [6]. VOPcF₁₆ films deposited onto quartz and silicon substrates were well organized and characterized by a predominantly co-facial parallel arrangement of molecules vertical to the surface.

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To improve the performance of CuPcF₁₆-based thin-film transistors, Yan et al. [7] employed an organic heterojunction buffer layer to decrease the contact resistance of organic/metal. The electron mobility is exponentially enhanced from 4.2×10^{-2} to 7.6×10^{-2} cm²/V·s. CuPcF₁₆-based transparent OTFTs based on Ag/LiF bilayer transparent S/D electrodes with good electron mobility of 1.31×10^{-2} cm²/V·s has been reported [8]. Highly ordered, continuous and large-size organic semiconductor films are favorable for charge transport in optoelectronic devices. Weak epitaxy growth (WEG) behavior and mechanism of CuPcF₁₆ on *p*-sexiphenyl (*p*-6P) thin film were deeply studied by Yan research group [9-11]. A high-quality CuPcF₁₆ films were obtained successfully by the method and the mobility of CuPcF₁₆-based OTFTs was greatly improved. To investigate the effect of axially coordinated ligand(s) on the semiconducting properties of phthalocyanine complexes, density functional theory (DFT) calculations were carried out in terms of the HOMO and LUMO energy of SnPcCl₂ and SnPc [12]. The calculated results indicate that functionalizing p-type metal phthalocyanine semiconductors with axially coordinated electron-withdrawing ligand(s) is a promising way toward n-type semiconductor molecular materials.

In this paper, axially coordinated Tin (IV) Dichloride hexadecafluorophthalocyanine (SnPcCl₂F₁₆, shown in Fig. 1) was synthesized and its optical, electrochemical and thermal properties were characterized. Especially SnPcCl₂F₁₆-based thin film transistor was prepared by inserting a *p*-sexiphenyl as the inducing layer and their electrical characteristics were also investigated.

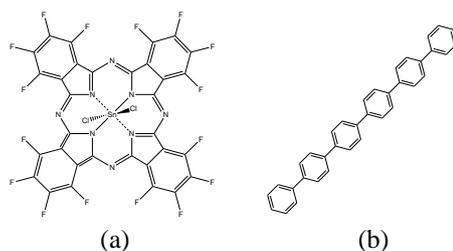


Fig. 1. Molecular structure of (a) SnPcCl₂F₁₆ and (b) *p*-6p.

2. Experiment

For the synthesis of SnPcCl₂F₁₆, tetrafluorophthalonitric and Tin (II) chloride dehydrate in an equimolar 4:1 ratio were intensively mixed in a mortar. The mixture was filled in a glass vessel and sealed under vacuum (1.33×10^{-3} Pa). After heating for 8 h at 240 °C the purple product was washed with ethanol and acetone to remove the soluble organic admixture. The resulting purple product with yield of 48.2% after purification by concentrated sulfuric acid was identified as SnPcCl₂F₁₆. IR (KBr) 1637, 1523, 1154, 832 and 765 cm⁻¹. MS (TOF, Methanol) *m/e* 955.62 (M-Cl). The SnPcCl₂F₁₆/*p*-6p thin film transistor configuration is given in Fig. 2. The device was prepared with the compound SnPcCl₂F₁₆ and a rod-like conjugated oligomer *p*-6p molecule. A *p*-6p thin film with 6nm thickness was first deposited on a SiO₂ substrate at 180 °C, and then a 30 nm thick layer of SnPcCl₂F₁₆ was deposited on top of the *p*-6p surface by thermal vacuum deposition. Finally, Au source and drain electrodes with 30 nm thickness were prepared by thermal deposition with a shadow mask defining channel width (*W*) and length (*L*) of 6000 μm and 200 μm, respectively. The output and transfer characteristics of the transistors were measured with two Keithley 2400 source-measurement units under ambient conditions at room temperature.

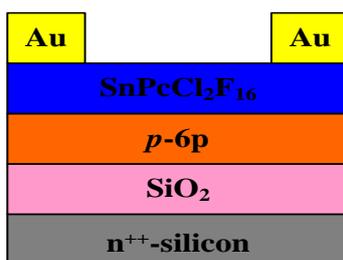


Fig. 2. The device configurations of $\text{SnPcCl}_2\text{F}_{16}/p\text{-}6p$ thin film transistors.

3. Results and discussion

3.1. UV-vis absorption spectra

Fig. 3 shows the UV-vis absorption spectra of $5 \times 10^{-5} \text{ mol L}^{-1}$ $\text{SnPcCl}_2\text{F}_{16}$ solutions in 1, 2-dichlorobenzene (DCB), tetrahydrofuran (THF) and dimethylformamide (DMF), respectively. The absorption spectra were measured by an EVOLUTION300 spectrometer. Absorption maxima for Q band are seen at 717 nm with shoulder peaks at 644 nm and 682 nm for $\text{SnPcCl}_2\text{F}_{16}$ dissolved in DCB and maximum absorption peak at 705, 700 and 698 nm for $\text{SnPcCl}_2\text{F}_{16}$ solution in THF, pyridine and DMF, respectively. With the increase of the polarity of solvents, the Q band shift to a shorter wave length to some extent, which originates from the increasement of the transition energy gap in the $\pi\text{-}\pi^*$ transition system. From Fig.3, the optical gap energy can be obtained from the edge of absorption band [13, 14]. The absorption edge of $\text{SnPcCl}_2\text{F}_{16}$ in DMF is found around 757 nm, from which the optical band gap energy of $\text{SnPcCl}_2\text{F}_{16}$, E_g , is estimated to be 1.64 eV.

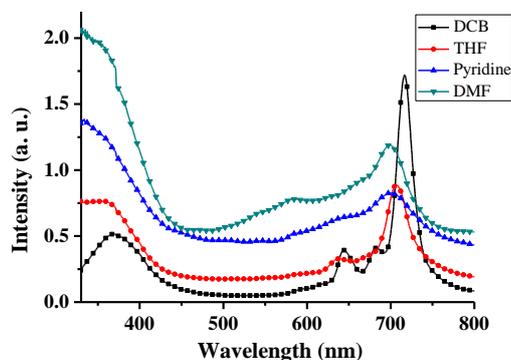


Fig. 3. The UV-vis spectra of $\text{SnPcCl}_2\text{F}_{16}$ in different solvents.

3.2 C-V curve

Solution cyclic voltammetry (CV) was employed to investigate the electrons transport ability and electrochemical properties of the $\text{SnPcCl}_2\text{F}_{16}$ compound. The cyclic voltammogram (Fig. 4) were collected on a CHI760E electrochemistry workstation at room temperature in DMF measured against a saturated calomel electrode (SCE) with tetrabutylammonium perchlorate (Bu_4NClO_4 , 0.10 M) as the supporting electrolyte. As shown in Fig. 4, the chemical oxidation and reduction peaks of $E_{\text{OX}} = -0.80 \text{ V}$ and $E_{\text{RE}} = -0.90 \text{ V}$ (versus standard calomel electrode, SCE) are observed. The reductive process started at -0.70 V . The energy level of the lowest unoccupied

molecular orbital, E_{LUMO} , can be estimated from the reductive onset potential to be -4.04 eV [15, 16]. The low LUMO energy level is favorable for electron injection and transport; in other words, $\text{SnPcCl}_2\text{F}_{16}$ should be a good electron transport material. The energy level of the highest occupied molecular orbital, E_{HOMO} , can be estimated by adding E_g from E_{LUMO} as determined by the electrochemistry. This leads to an estimation of E_{HOMO} to be -5.68 eV for $\text{SnPcCl}_2\text{F}_{16}$.

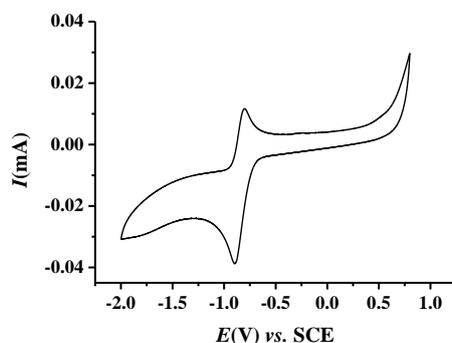


Fig. 4. Cyclic voltammogram of $\text{SnPcCl}_2\text{F}_{16}$ in DMF.

3.3. Thermal properties

The thermal properties of $\text{SnPcCl}_2\text{F}_{16}$ were characterized by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The TGA curve was measured by a TG 209 F3 thermo gravimetric analyzer. $\text{SnPcCl}_2\text{F}_{16}$ is relative stable and the mass loss is less than 10% below 100 °C. TGA measurements indicate that $\text{SnPcCl}_2\text{F}_{16}$ has high decomposition temperature of 471 °C (Td, correspond to a 10% mass loss, Fig. 5). $\text{SnPcCl}_2\text{F}_{16}$ exhibits excellent thermal stability and so its semiconductor thin film can be prepared by thermal deposition technique.

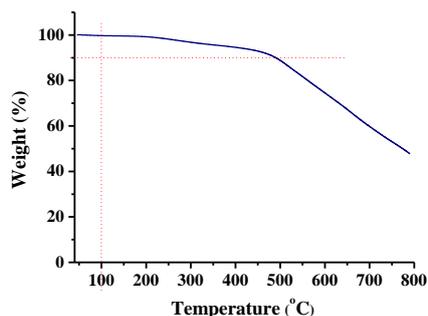


Fig. 5. TGA curves of $\text{SnPcCl}_2\text{F}_{16}$.

3.4 XRD of $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ film

Fig. 6 shows the XRD pattern of the $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ thin film. The X-ray diffraction was performed in a Rigaku D/max 2500 PC X-ray diffractometer with a Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å). The diffraction peaks of the $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ film at $2\theta = 6.97$, corresponding to d_{001} spacing of 12.68 Å, are observed. As indicated from the XRD pattern, the $\text{SnPcCl}_2\text{F}_{16}$ molecules stand up on the $p\text{-6p}$ layer and the intermolecular $\pi\text{-}\pi$ stacking direction parallel to the substrate [17-20].

For the films on the *p*-6P modified substrates, the presence of the (001) and (100) diffraction peaks implies formation of the crystalline films. This packing feature is beneficial to charge transport in OTFTS devices.

The growth behavior of the *p*-6p thin film has been studied systematically [10, 11]. A highly-ordered smooth *p*-6p ultrathin film can supply a high quality substrate for the growth of phthalocyanine molecules. The phthalocyanine molecules can be oriented on the inducing layer of rod-like *p*-6p molecules, which likely results from the geometrical channels of the *p*-6p layer surface and the dominant direction of semiconductor molecules on the *p*-6p thin film surface. And through the method of organic vapor deposition at high substrate temperature, organic phthalocyanine molecules can grow upright on the substrate. Thus the π - π conjugated direction is parallel to the *p*-6p layer.

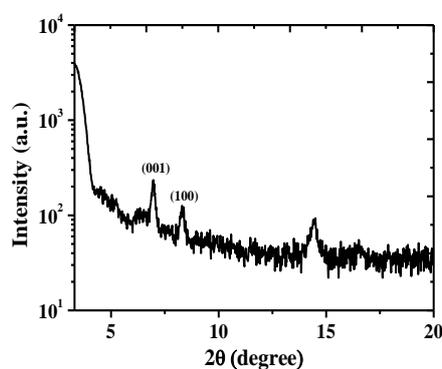


Fig. 6. X-ray diffraction spectra of $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ thin film.

3.5 AFM of $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ film

Atomic force microscopy (AFM) observations further investigated the morphology of $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ thin film, as shown in Figure 7. The $\text{SnPcCl}_2\text{F}_{16}$ film deposited on *p*-6P modified substrate consists of lamellar crystals, which is in agreement with the X-ray diffraction measurements. Meanwhile, these lamellar crystals are intimately connected, possibly because of coalescence at grain boundaries [20, 21]. All of the above results reveal that a highly ordered film with the intermolecular π - π stacking direction of $\text{SnPcCl}_2\text{F}_{16}$ molecules parallel to the substrate can be formed by inserting *p*-6p layer on the substrate.

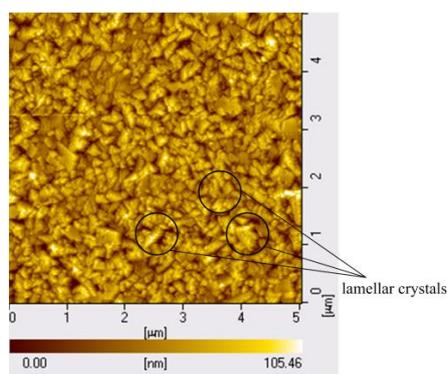


Fig. 7. Atomic force microscopy image of $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ thin film.

3.6. Current-voltage characteristics

The output characteristic curves of the $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ OTFTs are shown in Fig. 8 at different gate-source voltages (V_{GS}) from 0 to 50 V. When a positive bias of 50 V was applied to the gate and drain electrode, saturated drain current of about 0.17 μA in electron-accumulation mode was obtained. The $p\text{-6p}$ is a p-type semiconductor, while $\text{SnPcCl}_2\text{F}_{16}$ is an n-type semiconductor. Due to the heterojunction effect, the transistor presents ambipolar behavior.

Fig. 9 shows the transfer characteristics of the $\text{SnPcCl}_2\text{F}_{16}/p\text{-6p}$ OTFTs with different gate voltages at a fixed V_{DS} of 50 V. The field effect mobility was extracted from Fig. 10 in the saturation region ($V \geq (V_{\text{GS}} - V_{\text{T}})$) based on

$$I_{\text{DS}} = \frac{W}{2L} \mu C_i (V_{\text{GS}} - V_{\text{T}})^2 \quad (1)$$

Where I_{DS} is the drain-source current, W and L are the width and length of the channel, respectively, μ is the field-effect mobility, V_{GS} is the gate voltage and V_{T} is the threshold Voltage. The capacitance per unit area of the insulator (C_i) is 8 nF/cm^2 . According to the electrical properties, n -type conductivity of the $\text{SnPcCl}_2\text{F}_{16}$ semiconductor material was confirmed. The effect mobility of $0.85 \times 10^{-3} \text{ cm}^2/\text{V s}$ and the threshold Voltage of 7.62 V were extracted from the saturation region in Fig. 9.

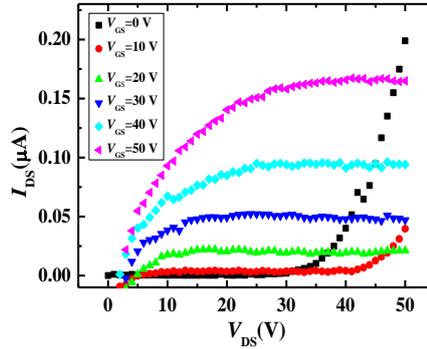


Fig. 8. Output characteristics of $\text{ZnPcF}_{16}/p\text{-6p}$ OTFTs.

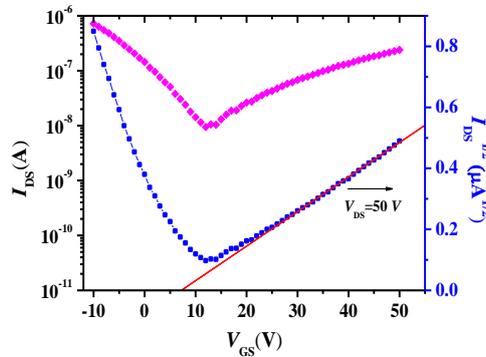


Fig. 9. Transfer characteristics of $\text{ZnPcF}_{16}/p\text{-6p}$ OTFTs at a fixed V_{DS} (50 V).

4. Conclusions

In summary, an *n*-type semiconductor material (SnPcCl₂F₁₆) with low LUMO energy level was synthesized. The electronic property was studied by UV-vis absorption and cyclic voltammetry methods. The SnPcCl₂F₁₆-based OTFTs using *p*-6p as the inducing layer was fabricated by the physical vapor deposition technique. The electrical properties of the OTFTs were investigated and *n*-type of conductivity was confirmed. And the charge carrier field-effect mobility of the SnPcCl₂F₁₆/*p*-6p OTFTs was $0.85 \times 10^{-3} \text{ cm}^2/\text{V s}$. The stable SnPcCl₂F₁₆ compound with high mobility will be a promising material for optical and electronic devices application.

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